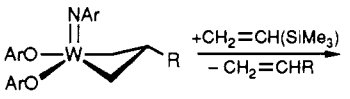
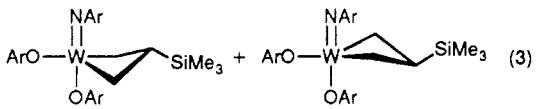
ethylene. **3a** clearly is more stable than **1a**; in the presence of excess ethylene **1a** rapidly gives **1c** and *tert*-butylethylene at temperatures above −20 °C. Square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(O\text{-}t\text{-}Bu)_2$ (**3b**) can be prepared from **3a** and several equivalents of ethylene in the presence of a large excess of *tert*-butylethylene, but the reaction requires several hours at 25 °C.[8] Due to its extreme solubility in hydrocarbons, we have thus far been unable to isolate **3b** in pure form and in good yield.

The reaction between **2b** and ethylene to give **2c** and *tert*-butylethylene is zero-order in ethylene and first-order in tungsten between 9 and 34 °C with $\Delta H^{\ddagger} = 19.8$ (4) kcal mol^{-1}, $\Delta S^{\ddagger} = -6$ (1) eu,[9] and $\Delta G^{\ddagger}_{298} = 21.6$ (7) kcal mol^{-1}. These results strongly contrast with the relative stability of **3a** and **3b** toward loss of *tert*-butylethylene in the presence of ethylene to give **3c**.

The nature of the substituents on the metallacycle ligand also influences the metallacycle's core geometry. As shown in eq 3, addition of vinyltrimethylsilane to square-pyramidal **2b** or fluxional **2c** yields two *trigonal-bipyramidal* isomers according to NMR studies in an approximately 2:1 ratio that we assign as **2d(*trans*)** and **2d(*cis*)**.[10] The formation of two isomers can be rationalized on the basis of little difference in size between the axial NAr and axial OAr ligands.



2b (R = *t*-Bu)
2c (R = H)



2d(trans) **2d(cis)** (3)

Our preliminary conclusions are that (i) the basic geometry of tungstacycles of this type sensitively depends upon the nature of the OR ligands and ring substituents and (ii) the barrier to interconversion of TBP and SP forms can be substantial. Detailed kinetic studies of these systems are now under way in order to determine how the core geometry of a tungstacyclobutane complex is related to its tendency to lose an olefin and to metathesize olefins. The results of these studies should be interesting to compare with those obtained for titanacyclobutane complexes where electron-donating substituents on the Cp ring stabilize the titanacycle and only the pseudotetrahedral core geometry is possible.[11]

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 84-02892) and the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292). J.F. thanks the National Science Foundation for a predoctoral fellowship.

Registry No. **1a**, 121211-74-3; **1b**, 121211-75-4; **1c(SP)**, 121211-76-5; **1c(TBP)**, 121251-51-2; **2b**, 121211-77-6; **2c(SP)**, 121211-78-7; **2c(TBP)**, 121251-52-3; **2d(trans)**, 121211-82-3; **2d(cis)**, 121251-53-4; **3a**, 121211-79-8; **3b**, 121211-80-1; **3c**, 121211-81-2; $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$, 107440-83-5; $CH_2{=}CH(t\text{-}Bu)$, 558-37-2; C_2H_4, 74-85-1; $^{13}C_2H_4$, 51915-19-6; $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$, 109678-83-3; $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$, 107440-84-6; $CH_2{=}CH(SiMe_3)$, 754-05-2.

Supplementary Material Available: A completely labeled ORTEP drawing of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ and tables of final positional and thermal parameters (3 pages); a listing of final observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

(8) Ethylene (2.2 mmol) was added via vacuum transfer to a solution of 250 mg (0.434 mmol) of $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ and 1.40 mL (6.51 mmol) of *tert*-butylethylene in 3.0 mL of pentane. After the solution had been stirred at 25 °C for 23 h, it was concentrated to a volume of ~0.5 mL and cooled to −40 °C. The orange solid that precipitated was recrystallized a second time from minimal pentane at −40 °C to afford 73 mg (0.121 mmol, 28%) of **3b** as bright yellow solid.

(9) (a) A recent paper[9b] reported kinetic studies of related *cationic* five-coordinate tungstacyclobutane complexes prepared with norbornene.[9c] Rate-limiting ring opening was found to have essentially the same $\Delta S^{\ddagger}$ as that reported here. It is interesting to note that according to the chemical shifts of the ring carbon atoms in one metallacycle (152.5, 141.6, and 25.6 ppm[9c]) it would appear to be a trigonal bipyramid with all resonances shifted downfield in response to the positive charge. (b) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1164. (c) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899.

(10) A solution of 120 mg (0.148 mmol) of $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ (**2b**) and 107 μL (0.745 mmol) of vinyltrimethylsilane in 5 mL of pentane was stirred at 25 °C for 2 h. Volatiles were removed in vacuo to afford an orange foam which was recrystallized from pentane at −40 °C to afford 82 mg (0.099 mmol, 67%) of **2d** as a yellow powder. The same compound can also be prepared by adding ~3 equiv of ethylene to $W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$, stirring the solution for 30 min at 25 °C, and then adding 5 equiv of vinyltrimethylsilane to the reaction mixture. For **2d(trans)**: $\delta(H_\alpha) = 4.87, 4.49$; $\delta(H_\beta) = -1.13$, $\delta(C_\alpha) = 100.5$, $\delta(C_\beta) = -0.99$. For **2d(cis)**: $\delta(H_\alpha) = 5.24, 4.20$; $\delta(H_\beta) = -1.23$, $\delta(C_\alpha) = 99.6$, $\delta(C_\beta) = -0.63$. Calcd for $WC_{42}H_{65}NO_2Si$: C, 60.93; H, 7.91. Found: C, 60.75; H, 7.95.

(11) (a) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406. (b) Hawkins, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2821. (c) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

η^4-*s*-*trans*-1,3-Dienes as Ligands for Cationic Molybdenum Centers

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Summary: Reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ with $Me_3SiOCH{=}CHCH{=}CH_2$ affords $[Mo\{endo\text{-}syn\text{-}\eta^3\text{-}1\text{-}C_3H_4CHO\}(CO)_2(\eta^5\text{-}C_5Me_5)]$, $[Mo\{exo\text{-}syn\text{-}\eta^3\text{-}1\text{-}C_3H_4CHO\}(CO)_2(\eta^5\text{-}C_5Me_5)]$, and $[Mo\{exo\text{-}anti\text{-}\eta^3\text{-}1\text{-}C_5H_4CHO\}(CO)_2(\eta^5\text{-}C_5Me_5)]$, which on treatment with the Wittig reagent Ph_3PCH_2 afford the corresponding η^3-pentadienyl complexes; protonation of both types of complexes at low temperature provides evidence for the formation of cationic η^4-*s*-*trans*-1,3-diene complexes.

The η^4-*s*-*cis*-1,3-diene ligand has played an important role in the development of organotransition-metal chemistry.[1] Recently, interest in 1,3-dienes as ligands has been further stimulated by the isolation and structural characterization of neutral complexes carrying η^4-*s*-*trans*-1,3-diene ligands.[2,3] Since it is likely that a different reactivity

(1) *Principles and Applications of Organotransition Metal Chemistry*; Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., Eds.; University Science Books: Mill Valley, CA, 1987.

(2) (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6433. (b) Nakamura, A.; Yasuda, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Erker, G.; Krüger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1 and references therein. (d) Okamoto, T.; Yasuda, H.; Nakamura, Y.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

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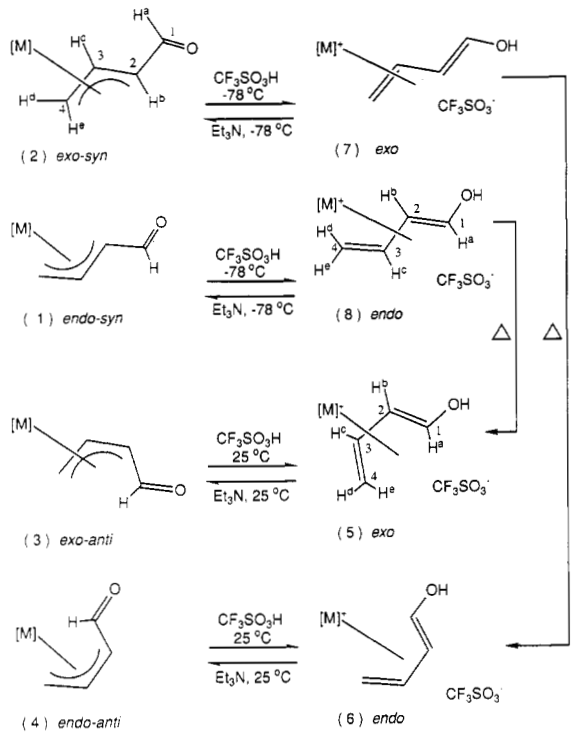
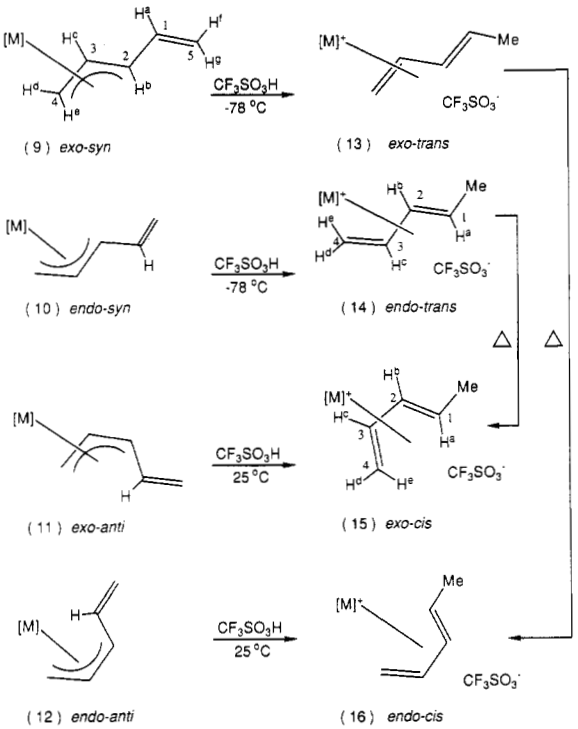
Scheme I[a]



[a] [M] = $[Mo(CO)_2(\eta^5\text{-}C_5Me_5)]$. Exo and endo refer to the relative stereochemical arrangement of the $\eta^5\text{-}C_5Me_5$ and allyl or diene ligand.

Scheme II[a]



[a] [M] = $[Mo(CO)_2(\eta^5\text{-}C_5Me_5)]$.

pattern will be associated with this bonding mode from that found with η^4-*s-cis*-1,3-dienes, it was interesting to obtain evidence for the existence of reactive cations of the type $[Mo(CO)_2(\eta^4\text{-}s\text{-}trans\text{-}1,3\text{-diene})(\eta^5\text{-}C_5Me_5)]^+$.

We have previously reported[4] that reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ with 1-((trimethylsilyl)oxy)cyclohexa-1,3-diene results in complexation, followed by desilylation with the formation in high yield of the 4-oxo-substituted η^3-cyclohexenyl complex $[Mo(\eta^3\text{-}C_6H_7O)(CO)_2(\eta^5\text{-}C_9H_7)]$. It was important to extend this chemistry to acyclic systems, and thus in order to avoid[5] complications arising from exo/endo and cis/trans isomerization, which could arise via the Faller–Rosan[6] ring-flip process, we have examined the reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_5Me_5)][BF_4]$[7] with *trans/cis*-1-((trimethylsilyl)oxy)buta-1,3-diene.

At room temperature in dichloromethane solution two products were formed (2 days), which were readily separated by column chromatography on alumina. The major product (50%) was identified by IR and NMR spectroscopy[8] as a mixture (7:3) of the unusual aldehyde substi-

(3) (a) Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791. (b) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Burstein, B. E.; Gatter, M. *J. Am. Chem. Soc.* **1986**, *108*, 3843. (c) Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics* **1989**, *8*, 930.

(4) Green, M.; Greenfield, S. G.; Grimshire, M. J.; Kersting, M.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 97.

(5) In contrast with the corresponding $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_9H_7$ complexes the pentamethylcyclopentadienyl-substituted cations $[Mo(CO)_2(\eta^4\text{-}1,3\text{-diene})(\eta^5\text{-}C_5Me_5)][BF_4]$ do not readily undergo cis/trans isomerization about the 1-position of the 1,3-diene. See: Green, M.; Greenfield, S. G.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.

(6) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

(7) Selected spectroscopic data: ^1H NMR (CD_2Cl_2) δ 2.53 (s, 6 H, MeCN), 1.86 ppm (s, 15 H, C_5Me_5); IR (CH_2Cl_2), 1975, 1889 cm^{-1}.

(8) Selected spectroscopic data for compound **1**: ^1H NMR (CD_2Cl_2) δ 8.91 (d, 1 H, H^a, J_{ab} = 7.9 Hz), 4.34 (ddd, 1 H, H^c, J_{cb} = 8.3, J_{cd} = 6.4, J_{ce} = 10.6 Hz), 3.04 (d, 1 H, H^d, J_{dc} = 6.4 Hz), 1.87 (s, 15 H, C_5Me_5), 1.60 (dd, 1 H, H^b, J_{ba} = 7.9, J_{bc} = 8.3 Hz), 1.18 (d, 1 H, H^e, J_{ec} = 10.6 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 239.3 (CO), 238.9 (CO), 193.4 (C_1), 105.3 (C_5Me_5), 80.9 (C_3), 62.1 (C_2), 44.0 (C_4), 11.4 ppm (C_5Me_5); IR (CH_2Cl_2) 1958, 1878, 1666 cm^{-1}. Compound **2**: ^1H NMR (CD_2Cl_2) δ 8.83 (d, 1 H, H^a, J_{ab} = 8.4 Hz), 3.71 (ddd, 1 H, H^c, J_{cb} = 9.4, J_{cd} = 7.2, J_{ce} = 11.5 Hz), 2.09 (dd, 1 H, H^d, J_{dc} = 7.2 Hz), 1.91 (s, 15 H, C_5Me_5), 1.76 (dd, 1 H, H^b, J_{ba} = 8.4, J_{bc} = 9.4 Hz), 1.64 (dd, 1 H, H^e, J_{ec} = 11.5 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 241.7 (CO), 240.8 (CO), 195.3 (C_1), 104.1 (C_5Me_5), 91.3 (C_3), 64.9 (C_2), 47.6 (C_4), 10.8 ppm (C_5Me_5). Compound **3**: ^1H NMR (CD_2Cl_2) δ 7.00 (d, 1 H, H^a, J_{ab} = 7.8 Hz), 3.51 (ddd, 1 H, H^c, J_{cb} = 7.1, J_{cd} = 8.4, J_{ce} = 11.6 Hz), 3.42 (m, 1 H, H^b), 2.28 (ddd, 1 H, H^d, J_{dc} = 8.4 Hz), 1.88 (s, 15 H, C_5Me_5), 1.75 (dd, 1 H, H^e, J_{ec} = 11.6 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 237.7 (CO), 237.4 (CO), 184.8 (C_1), 105.0 (C_5Me_5), 80.2 (C_3), 65.1 (C_2), 42.5 (C_4), 10.5 ppm (C_5Me_5). Compound **5**: ^1H NMR (CD_2Cl_2, 298 K) δ 5.67 (d, 1 H, H^a, J_{ab} = 9.3 Hz), 4.30 (dd, 1 H, H^b, J_{ba} = 9.3, J_{bc} = 6.3 Hz), 4.11 (ddd, 1 H, H^c, J_{cb} = 6.3, J_{cd} = 8.5, J_{ce} = 11.7 Hz), 2.20 (dd, 1 H, H^d, J_{dc} = 8.5 Hz), 1.94 (s, 15 H, C_5Me_5), 1.41 ppm (dd, 1 H, H^e, J_{ec} = 11.7 Hz); IR (CH_2Cl_2) 2000 s, 1933 s cm^{-1}. Compound **6**: ^1H NMR (CD_2Cl_2 298 K) δ 4.72 (dd, 1 H, H^b, J_{ba} = 9.2, J_{bc} = 6.3 Hz), 4.24 (ddd, 1 H, H^c, J_{cb} = 6.3, J_{cd} = 8.3, J_{ce} = 12.5 Hz), 2.27 (dd, 1 H, H^d, J_{dc} = 8.3 Hz), 1.98 (s, 15 H, C_5Me_5), 1.26 ppm (dd, 1 H, H^e, J_{ec} = 12.5 Hz). Compound **7**: ^1H NMR (CD_2Cl_2, 240 K), δ 6.79 (d, 1 H, H^a, J_{ab} = 10.8 Hz), 3.35 (dd, 1 H, H^e, J_{ec} = 11.4 Hz), 3.22 (ddd, 1 H, H^c, J_{cb} = 7.7, J_{cd} = 6.9, J_{ce} = 11.4 Hz), 3.07 (dd, 1 H, H^b, J_{ba} = 10.8, J_{bc} = 7.7 Hz), 2.72 (dd, 1 H, H^d, J_{dc} = 6.9 Hz), 1.82 ppm (s, 15 H, C_5Me_5). Compound **8**: ^1H NMR (CD_2Cl_2, 240 K) δ 7.61 (d, 1 H, H^a, J_{ab} = 10.1 Hz), 4.13 (ddd, 1 H, H^c, J_{cb} = 7.4, J_{cd} = 6.4, J_{ce} = 11.5 Hz), 3.65 (d, 1 H, H^d, J_{dc} = 6.4 Hz), 2.56 (d, 1 H, H^e, J_{ec} = 11.5 Hz), 2.53 (dd, 1 H, H^b, J_{ba} = 10.1, J_{bc} = 7.4 Hz), 1.88 ppm (s, 15 H, C_5Me_5). Compound **9**: ^1H NMR (CD_2Cl_2) δ 5.75 (ddd, 1 H, H^a, J_{ab} = 10.5 Hz), 5.13 (dd, 1 H, H^f), 4.81 (dd, 1 H, H^g), 3.20 (ddd, 1 H, H^c, J_{cb} = 10.3, J_{cd} = 7.1, J_{ce} = 10.1 Hz), 2.16 (dd, 1 H, H^b, J_{ba} = 10.5, J_{bc} = 10.3 Hz), 1.76 (s, 15 H, C_5Me_5), 1.04 (dd, 1 H, H^e, J_{ec} = 10.1 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 242.7 (CO), 240.1 (CO), 137.8 (C_1), 110.8 (C_5), 104.2 (C_5Me_5), 77.2 (C_3), 67.3 (C_2), 39.1 (C_4), 11.1 ppm (C_5Me_5). Compound **10**: ^1H NMR (CD_2Cl_2) δ 6.13 (ddd, 1 H, H^a, J_{ab} = 10.2 Hz), 4.99 (dd, 1 H, H^f), 4.72 (dd, 1 H, H^g), 3.93 (ddd, 1 H, H^c, J_{cb} = 9.9, J_{cd} = 6.3, J_{ce} = 10.0 Hz), 2.80 (d, 1 H, H^d, J_{dc} = 6.3 Hz), 1.68 (s, 15 H, C_5Me_5), 0.55 ppm (d, 1 H, H^e, J_{ec} = 10.0 Hz). Compound **13**: ^1H NMR (CD_2Cl_2, 213 K) δ 4.24 (dq, 1 H, H^a, J_{ab} = 12.6 Hz), 3.79 (d, 1 H, H^e), 3.48 (dd, 1 H, H^b, J_{ba} = 12.6, J_{bc} = 6.7 Hz), 3.19 (m, 1 H, H^d), 3.17 (m, 1 H, H^c), 1.94 (d, 3 H, Me), 1.90 (s, 15 H, C_5Me_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 228 K, gate decoupled) δ 233.2 (s, CO), 225.6 (s, CO), 119.0 (q, CF_3SO_3, J(CF) = 317.8 Hz), 108.7 (s, C_5Me_5), 101.6 (d, C_1, J(CH) = 152.8 Hz), 94.6 (d, C_2 or C_3, J(CH) = 170.9 Hz), 87.7 (d, C_2 or C_3, J(CH) = 171.3 Hz), 68.8 (t, C_4, J(CH) = 165.3 Hz), 18.4 (q, Me, J(CH) = 129.6 Hz), 10.3 ppm (q, C_5Me_5, J(CH) = 129.0 Hz). Compound **14**: ^1H NMR (CD_2Cl_2, 213 K) δ 4.99 (dq, 1 H, H^a, J_{ab} = 12.0 Hz), 4.24 (d, 1 H, H^d, J_{de} = 6.8 Hz), 3.65 (dt, 1 H, H^c, J_{cb}, J_{cd} = 7.0, J_{ce} = 12.9 Hz), 3.34 (dd, 1 H, H^b, J_{ba} = 12.0, J_{bc} = 7.5 Hz), 3.24 (m, 1 H, H^e), 1.93 (s, 15 H, C_5Me_5), 1.90 ppm (d, 3 H, Me). Compound **16**: ^1H NMR (CD_2Cl_2, 298 K) δ 6.05 (ddd, 1 H, H^c, J_{cb} = 5.2, J_{cd} = 7.5 Hz), 5.82 (dd, 1 H, H^b, J_{ba} = 10.0, J_{bc} = 5.2 Hz), 2.65 (d, 1 H, H^d, J_{de} = 10.4 Hz), 2.02 (s, 15 H, C_5Me_5), 1.68 (d, 3 H, Me), 1.10 ppm (d, 1 H, H^e, J_{ed} = 10.4 Hz).

tuted η^3-allyl complexes [Mo{*endo-syn*-η^3-1-C_3H_4CHO}-$(CO)_2(\eta^5$-$C_5Me_5)$] (1)[9] and [Mo{*exo-syn*-η^3-1-C_3H_4CHO}-$(CO)_2(\eta^5$-$C_5Me_5)$] (2), the minor product (4%) being [Mo{*exo-anti*-η^3-1-C_3H_4CHO}$(CO)_2(\eta^5$-$C_5Me_5)$] (3) (see Scheme I).

To gain insight into the chemistry of these functionalized η^3-allyls, their reactivity toward strong acids was examined. The low-temperature (−78 °C, CF_3SO_3H, CH_2Cl_2) protonation of the mixture of **1** and **2**, or the single isomer **3**, afforded respectively on room temperature workup either a mixture (7:3) of the exo and endo isomers of the *trans*-1-hydroxybuta-1,3-diene cationic complexes **5** and **6** or just **5**, in each case with a cisoid geometry about the C_2–C_3 axis (Scheme I). These, unlike the corresponding η^5-C_5H_5 and η^5-C_9H_7 complexes, are not interconvertible and do not isomerize into the η^4-*s-cis,cis*-1-hydroxybuta-1,3-diene cations. Addition of triethylamine to the mixture of **5** and **6** resulted in deprotonation, regenerating **1**, **2**, and **3**, but with **3**, i.e. the exo-anti isomer, now predominating. When **1** and **2** were protonated and then deprotonated at low temperature, only **1** and **2** were regenerated in the original ratio of 7:3 (Scheme I).

The conversion of **5** into **3** can be seen to proceed without alteration to the overall stereochemistry of the carbon skeleton of the coordinated ligand. This was found to be equally applicable to the reverse reaction, thus establishing the nature of the interconversions as being exclusively *anti*-η^3-allyl aldehyde $\rightleftharpoons$ η^4-*s-cis*-1,3-hydroxydiene and suggesting that a similar retention of stereochemistry occurs on protonation of the *syn*-η^3-allyl aldehydes leading to the formation of cationic η^4-*s-trans*-1,3-diene species, which on warmup isomerize to the isolated η^4-*s-cis*-1,3-diene cations. In order to explore this interesting idea, the mixture of **1** and **2** was protonated at low temperature (CF_3SO_3H, CD_2Cl_2, −78 °C) in an NMR tube, resulting in a quantitative conversion into two new cationic species. These were identified unambiguously by ^1H NMR spectroscopy[8] as the η^4-*s-trans*-1-hydroxybuta-1,3-diene complexes **7** and **8** (Scheme I), thereby confirming the predicted *syn*-allyl $\rightleftharpoons$ transoid 1,3-diene relationship. Complexes **7** and **8** were shown to be stable in solution below ca. −40 °C, isomerizing irreversibly at more elevated temperatures into the corresponding cisoid species **6** and **5**, respectively. A comparison between the ^1H NMR spectroscopic data reveals the following points of note. A decrease in the magnitude of ^3J(HH) across the C_2–C_3 bond is observed [**7**, 7.7 Hz; **8**, 7.4 Hz; **5**, 6.3 Hz; **6**, 6.3 Hz] upon isomerization (transoid to cisoid) as might be expected.[2,3] Secondly there is a marked upfield shift of the "inside" protons (H^a and H^e) in the cisoid complexes, relative to the values obtained from the elongated transoid analogues.

These novel aldehyde substituted η^3-allyls are also potential precursors of pentadienyl complexes, a class of compounds which are currently attracting attention.[10] Reaction (thf, −78 °C) of **1** and **2** with the Wittig reagent Ph_3PCH_2 afforded a mixture of the *exo*- and *endo-syn*-η^3-pentadienyl complexes **9** and **10** in a ratio of 7:3, i.e. opposite to the exo/endo ratio of the precursor aldehyde-substituted species. A similar reaction between the exo-anti complex **3** and Ph_3PCH_2 afforded only the *exo-anti*-η^3-pentadienyl complex **11**. Thus, these observations establish a new and possibly general synthetic approach to η^3-pentadienyl complexes.

It was of obvious importance to examine the protonation of these η^3-pentadienyl-substituted species. Protonation (−78 °C, CF_3SO_3H, CH_2Cl_2) of the mixture of **9** and **10** followed by room-temperature workup afforded a mixture (7:3) of **16** and **15**, respectively, there being no evidence for the formation of the corresponding η^4-*s-cis,cis*-penta-1,3-diene cations. Similarly, protonation of **11** gave only **15** (Scheme II). Importantly, upon repetition of the protonation reaction in CD_2Cl_2 solution, with the progress of the reaction being monitored by ^1H NMR, it was clear that at low temperature the mixture of **9** and **10** gave only the cations **13** and **14** (*exo*-η^4-*s-trans,trans*-penta-1,3-diene and *endo*-η^4-*s-trans,trans*-penta-1,3-diene substituted species) and that only on warming to −40 °C did these undergo irreversible thermal isomerization to the thermodynamically more stable η^4-*s-cis,trans*-penta-1,3-diene cations **15** and **16**.

Thus in conclusion, these observations show that η^4-*s-trans*-1,3-dienes can in fact be stabilized by the cationic metal fragment $Mo(CO)_2(\eta^5$-$C_5Me_5)$. The establishment of regioselectivity for the low-temperature reactions of these η^4-*s-trans*-penta-1,3-diene cations with nucleophilic reagents will be of particular interest.

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Registry No. **1**, 121987-64-2; **2**, 122087-46-1; **3**, 122087-47-2; **5**, 121987-66-4; **6**, 122087-49-4; **7**, 122087-51-8; **8**, 122087-53-0; **9**, 121987-67-5; **10**, 122087-54-1; **11**, 122087-55-2; **13**, 121987-69-7; **14**, 122087-57-4; **15**, 122087-59-6; **16**, 122087-61-0; [Mo-$(NCMe)_2(CO)_2(\eta^5$-$C_5Me_5)$][BF_4], 121987-71-1; Ph_3PCH_2, 3487-44-3; *trans*/*cis*-1-((trimethylsilyl)oxy)buta-1,3-diene, 6651-43-0.

(9) A single-crystal X-ray diffraction study (Bates, P.; Green, M.; Hursthouse, M.; Waring, T., unpublished observations) with the related complex [Ru{*exo-syn*-η^3-1-C_3H_4CO}$(CO)(\eta^5$-$C_5H_5)$] shows that the carbonyl group of the aldehyde functionality is oriented in the same way as is illustrated in Scheme I for complex **2** and that possibly related to this, there was evidence for π-electron delocalization.

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P–C Bond Activation of Triphenylphosphine. Formation of a Dinuclear μ-η^2:η^2-Benzene Complex of Ruthenium

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Summary: The dinuclear tetrahydride $(\eta^5$-$C_5Me_5)Ru(\mu$-$H)_4Ru(\eta^5$-$C_5Me_5)$ reacts with triphenylphosphine to give $(\eta^5$-$C_5Me_5)Ru(\mu$-$PPh_2)(\mu$-$H)(\mu$-η^2:η^2-$C_6H_6)Ru(\eta^5$-$C_5Me_5)$. The structure of the complex has been determined by a single-crystal X-ray diffraction study, which shows the complex to have an η^4-benzene as a bridging ligand.

In the preceding communication, we reported the synthesis of a novel tetrahydride-bridged dinuclear ruthenium complex, $(\eta^5$-$C_5Me_5)Ru(\mu$-$H)_4(\eta^5$-$C_5Me_5)$ (**1**),[1] and the ac-

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